

reduction of an ion gives rise to phenomena of very large capacity. which simulate the behavior of a condenser

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Molecular Size Distributions and Depolymerization Reactions in Polydisperse Systems

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When experimenting with long chain polymers it is desirable to use molecules which are all composed of the same number of monomeric elements. Since such a homogeneous system is difficult to prepare, one must often be satisfied with more or less heterogeneous mixtures. An indication of the molecular size distribution of this type of system can be obtained by applying statistical methods to the various molecular weights that can be determined experimentally.

If a long chain molecule in a system of N similar polymers consists of p monomeric elements or fundamental units (for example, the monomeric elements in cellulose are glucose units), it will be a p -mer and its molecular weight will be denoted by M_p . Letting n_p be the fraction of p -mers in the system and m the molecular weight of a monomeric element, Nn_p is the total number of p -mers and $M_p = mp$. Now any experimental method (such as chemical analysis, vapor or osmotic pressure measurements) which in effect involves the counting of molecules, measures the "number average" molecular weight

$$M_1 = \frac{\sum_p M_p n_p}{\sum_p n_p} \quad (1)$$

The average value resulting from a procedure depending on weights of the molecules (*e. g.*, Staudinger's viscosity method) is given by the "weight average" molecular weight:

$$M_2 = \frac{\sum_p M_p^2 n_p}{\sum_p M_p n_p} \quad (2)$$

Sedimentation equilibrium measurements in an ultracentrifuge make available the "z-average" molecular weight¹

$$M_3 = \frac{\sum_p M_p^3 n_p}{\sum_p M_p^2 n_p} \quad (3)$$

It is now apparent from (1), (2) and (3) that the moments of the distribution function, n_p , the i -th of which is

$$\mu_i = \sum_p p^i n_p \quad (4)$$

can be expressed in terms of the M_i 's

$$M_i = \frac{\sum_p M_p^i n_p}{\sum_p M_p^{i-1} n_p} = m \frac{\sum_p p^i n_p}{\sum_p p^{i-1} n_p} = m \frac{\mu_i}{\mu_{i-1}} \quad (5)$$

or, since

$$\sum_p n_p = 1$$

$$\mu_i = M_1 M_2 \dots M_i / m^i \quad (6)$$

In a polydisperse system in which the molecular size distribution has a single maximum, this distribution might be almost normal. As has been discussed by Lansing and Kraemer,¹ a logarithmically normal distribution function is applicable when there is reason to believe that a strong deviation toward the high molecular weight components exists. Since only two moments are required to calculate normal and logarithmically normal distribution functions, they do not make use of all the possible experimental information. We will now proceed to derive a distribution function which involves all the measurable moments, and then we will develop a theory of depolymerization of polydisperse systems with arbitrary initial distributions.

Almost Normal Molecular Size Distributions.

—The fraction of p -mers in a system with a normal distribution² of molecular sizes is

$$n_0(p) = e^{-(\mu_1 - p)^2 / 2\sigma^2} / \sigma \sqrt{2\pi} \quad (7)$$

where μ_1 is the average degree of polymerization or first moment of the distribution and σ^2 is the mean deviation, $\mu_2 - \mu_1^2$. Since any continuous function, $f(p)$, such that $\int_{-\infty}^{\infty} |f(p)|^2 dp < \infty$, can be expanded as a product of a Gaussian error function (7) and a linear combination of Hermite polynomials, an almost normal distribution function can be written

$$n_p = \sum_{n=0}^{\infty} c_n n_0(p) H_n \left(\frac{\mu_1 - p}{\sigma} \right) \quad (8)$$

(2) The treatment for logarithmically normal distributions similar to those of Lansing and Kraemer¹ but involving three observable moments proceeds in a similar manner. See, for example, A. Fisher, "The Mathematical Theory of Probabilities," New York, N. Y., 1926, p. 235.

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(1) See Kraemer's article on polydisperse systems in "The Ultracentrifuge," edited by Svedberg and Pedersen, Oxford Press (1940); or Lansing and Kraemer, THIS JOURNAL, **57**, 1369 (1935).

The first few Hermite polynomials are

$$\begin{aligned} H_0(z) &= 1 \\ H_1(z) &= z \\ H_2(z) &= z^2 - 1 \\ H_3(z) &= z^3 - 3z \end{aligned}$$

and all these polynomials satisfy the ortho normalization condition

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} H_n(z) H_m(z) e^{-z^2/2} dz = \sqrt{n!m!} \delta_{nm} \quad (9a)$$

$\delta_{nm} = 1$ if $m = n$ and zero otherwise. Substituting $z = (\mu_1 - p)/\sigma$ in (9a):

$$\int_{-\infty}^{\infty} H_n\left(\frac{\mu_1 - p}{\sigma}\right) H_m\left(\frac{\mu_1 - p}{\sigma}\right) n_0(p) dp = \sqrt{n!m!} \delta_{nm} \quad (9b)$$

Thus multiplication of both sides of (8) by $H_m\left(\frac{\mu_1 - p}{\sigma}\right) dp$ and integration from $p = -\infty$ to $p = +\infty$ yields the constants

$$m!c_m = \int_{-\infty}^{\infty} n_p H_m\left(\frac{\mu_1 - p}{\sigma}\right) dp \quad (10)$$

To translate the c 's into experimental moments and average molecular weights we proceed as follows

$$\begin{aligned} c_0 &= \int_{-\infty}^{\infty} H_0 n_p dp = \int_{-\infty}^{\infty} n_p dp = 1 \\ c_1 &= \int_{-\infty}^{\infty} \left(\frac{\mu_1 - p}{\sigma}\right) n_p dp = \frac{\mu_1 - \mu_1}{\sigma} = 0 \\ 2!c_2 &= \int_{-\infty}^{\infty} \left[\left(\frac{\mu_1 - p}{\sigma}\right)^2 - 1\right] n_p dp = \frac{-\mu_1 + \mu_2}{\sigma^2} - 1 = 0 \\ 3!c_3 &= \int_{-\infty}^{\infty} \left(\frac{\mu_1^3}{\sigma^3} - \frac{3p\mu_1^2}{\sigma^3} + \frac{3p^2\mu_1}{\sigma^3} - \frac{p^3}{\sigma^3} - \frac{3\mu_1}{\sigma} + \frac{3p}{\sigma}\right) n_p dp \\ &= -\frac{2\mu_3 - 3\mu_1\mu_2 + \mu_3}{\sigma^3} \end{aligned}$$

Using these values for c_1 , c_2 and c_3 and abbreviating $\lambda_3 = 2\mu_3^3 - 3\mu_1\mu_2 + \mu_3$, n_p becomes

$$n_p = \frac{e^{-(\mu_1 - p)^2/2\sigma^2}}{\sigma\sqrt{2\pi}} \left\{ 1 - \frac{\lambda_3}{3!\sigma^3} H_3\left(\frac{\mu_1 - p}{\sigma}\right) + \dots \right\} \quad (11)$$

Although it is possible in principle to determine moments higher than the third from ultracentrifuge analysis the errors would accumulate rapidly, so it would be advisable to cut off the expansion with the third Hermite polynomial; however, unless a system deviates radically from a normal one, (11) should be quite accurate. Actually the experimental moments $\mu_i = \mathbf{M}_1\mathbf{M}_2 \dots \mathbf{M}_i/m^i$ are sums, while the μ_i 's in equation (11) are integrals. But, inasmuch as the number of molecules to be averaged over is large, and since it is difficult to

differentiate experimentally between a molecule of say 300 monomeric elements and one of 301, the error introduced by replacing the sums by integrals is not large. The introduction of the various average molecular weights makes

$$n_p = \frac{e^{-(M_1/m - p)^2/2\sigma^2}}{\sigma\sqrt{2\pi}} \left\{ 1 - \frac{\lambda_3}{3!\sigma^3} H_3\left(\frac{M_1/m - p}{\sigma}\right) + \dots \right\} \quad (12)$$

$$\sigma^2 = \mathbf{M}_1(\mathbf{M}_2 - \mathbf{M}_1)/m^2$$

$$\lambda_3 = \mathbf{M}_1(2\mathbf{M}_1^2 - 3\mathbf{M}_1\mathbf{M}_2 + \mathbf{M}_2\mathbf{M}_3)/m^3$$

Physically, σ^2 gives an indication of the sharpness of the distribution in such a way that as σ increases, the distribution curve broadens, while the skewness or deviation from normal is indicated by λ_3 so that as $\lambda_3 \rightarrow 0$ the curve approaches a normal one. When λ_3 is negative, molecular sizes smaller than the most probable ones predominate over those less than the most probable, and *vice versa* for positive σ_3 . In Fig. 1 are plotted three distribution functions for systems with number average molecular weights $\mathbf{M}_1 = 350m$ and weight average molecular weights $\mathbf{M}_2 = 354m$. Curve (1) is the normal distribution which corresponds to $\lambda_3 = 0$. Curve (2) results from choosing a z -average molecular weight $\mathbf{M}_3 = 357m$. This choice makes $\lambda_3/6\sigma^3 = -0.359$, the negativness of which leads to a predomination of less than "most probable" molecular sizes. Curve (3) shows the long chain predomination that comes from choosing $\mathbf{M}_3 = 359m$. Here $\lambda_3/6\sigma^3 = +0.430$. The skewness is as delicate to small differences in \mathbf{M}_3 as it is in Fig. 1 only when the \mathbf{M}_3 's are close to the value which makes the curve normal.

Depolymerization of a Mixture of Long Polymers.—A complete investigation of the kinetics of decomposition of long chain molecules has two aspects: the time variation of the degree of depolymerization, and the distribution of various chain lengths at a given time for a given degree of depolymerization and a given initial distribution of chain lengths. The size distribution aspect has recently been analyzed³ for a system in which:

1. All initial molecules are of the same molecular weight.
2. The accessibility to reaction of a bond is independent of its position in a chain and independent of the length of its parent chain.
3. The bonds of all the chains in the mixture at any given time are equally accessible to reaction.

The difficulty of preparation of uniform samples

(3) Montroll and Simha, *J. Chem. Phys.*, **8**, 721 (1940). References to past work, experimental and theoretical, are given in this paper.

for depolymerization makes it desirable to eliminate the first assumption; so, using the results of the last section we will now investigate the degradation of mixtures with an arbitrary initial distribution and especially those whose initial distribution is almost normal.

If an initial material is homogeneous the depolymerization process can be studied by first developing a theory of the breaking of single molecules and then taking into account the distribution of breaks in the various chains. In such a manner it has been shown³ that if α , the degree of depolymerization, is defined as the probability of a given bond being split (*i. e.*, α is the ratio of the total number of bonds cut to the total number of bonds in the system), the average fraction of monomeric elements existing as components of t -mers in a system that was originally composed of $N(p + 1)$ -mers is

$$F_t(p, \alpha) = \frac{t(1 - \alpha)^{t-1}}{p + 1} [2 + (p - t)\alpha], t < p \quad (13a)$$

$$F_{p+1}(p, \alpha) = (1 - \alpha)^p$$

Since the total number of t -mers, $N_t(p, \alpha)$, is given by

$$N_t(p, \alpha) = NF_t(p, \alpha)(1 + p)/t$$

(13a) implies

$$N_t(p, \alpha) = N\alpha(1 - \alpha)^{t-1}[2 + (p - t)\alpha], t \leq p \quad (13b)$$

$$N_{p+1}(p, \alpha) = N(1 - \alpha)^p$$

Now consider the depolymerization of a system that initially consisted of N polymers distributed into Nn_1 monomers, Nn_2 dimers, . . . , Nn_p p -mers, . . . , in such a manner that conditions (2) and (3) remain valid throughout the degradation process. The total number of t -mers, $N_t(\alpha)$, when the degree of depolymerization is α , is the totality of t -mers generated from each of the original molecular species composed of t or more monomers. Thus

$$\begin{aligned} N_t(\alpha) &= \sum_{p+1=t}^{\infty} N_t(p, \alpha) \\ &= Nn_t(1 - \alpha)^{t-1} + \\ &\quad N \sum_{p+1=t+1}^{\infty} n_{p+1}\alpha(1 - \alpha)^{t-1}[2 + (p - t)\alpha] \end{aligned} \quad (14)$$

Let us assume that the initial material has an arbitrary size distribution in which the fraction of p -mers is

$$n_p = \frac{e^{-(\mu_1 - p)/2\sigma^2}}{\sigma\sqrt{2\pi}} \sum_{j=0}^{\infty} c_j H_j\left(\frac{\mu_1 - p}{\sigma}\right) \quad (15)$$

Then if we let $1 - \alpha = \beta$ and $(\mu_1 - p)/\sigma = z$

$$\begin{aligned} N_t(\alpha) &= n_t N \beta^{t-1} + \\ &\quad \frac{\alpha N \beta^{t-1}}{\sqrt{2\pi}} [2 + \alpha(\mu_1 - t)] \sum_{j=0}^{\infty} c_j \int_{-\infty}^{\infty} e^{-z^2/2} H_j(z) dz - \\ &\quad \frac{\alpha^2 N \beta^{t-1} \sigma}{\sqrt{2\pi}} \sum_{j=0}^{\infty} c_j \int_{-\infty}^{\infty} z e^{-z^2/2} H_j(z) dz \end{aligned} \quad (16)$$

In an almost normal distribution

$$\sum c_j H_j(z) = 1 - \frac{\lambda_3}{3! \sigma^3} H_3(z)$$

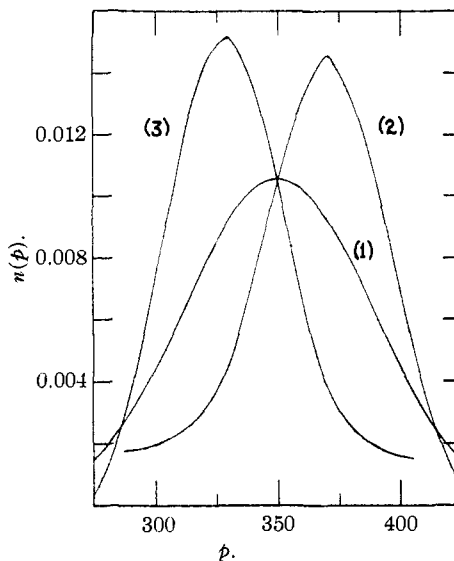


Fig. 1.—Three types of molecular size distributions

Since, as one can show by integration by parts⁴

$$\begin{aligned} \int_{-\infty}^A e^{-z^2/2} dz &= \sqrt{\frac{\pi}{2}} \left[1 + \Phi\left(\frac{A}{\sqrt{2}}\right) \right] \\ \int_{-\infty}^A z e^{-z^2/2} dz &= -e^{-A^2/2} \\ \int_{-\infty}^A H_2(z) e^{-z^2/2} dz &= (1 - A^2) e^{-A^2/2} = -H_2(A) e^{-A^2/2} \\ \int_{-\infty}^A z H_2(z) e^{-z^2/2} dz &= -A^3 e^{-A^2/2}, \end{aligned}$$

we have

$$\begin{aligned} N_t(\alpha) &= Nn_t \beta^{t-1} + \\ &\quad \frac{\alpha N \beta^{t-1}}{\sqrt{2\pi}} [2 + \alpha(\mu_1 - t)] \left\{ \sqrt{\frac{\pi}{2}} \left[1 + \Phi\left(\frac{\mu_1 - t}{\sqrt{2}\sigma}\right) \right] + \right. \\ &\quad \left. \frac{\lambda_3}{3! \sigma^3} H_2\left(\frac{\mu_1 - t}{\sigma}\right) e^{-(\mu_1 - t)^2/2\sigma^2} \right\} + \\ &\quad \frac{\alpha^2 \sigma N \beta^{t-1}}{\sqrt{2\pi}} e^{-(\mu_1 - t)^2/2\sigma^2} \left\{ 1 - \frac{\lambda_3}{3! \sigma^3} \left(\frac{\mu_1 - t}{\sigma}\right)^3 \right\} \end{aligned} \quad (17)$$

$$(4) \quad \Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx. \quad \text{For } x \ll 1:$$

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{118} + \frac{x^5}{215} - \dots \right)$$

$$\text{For } x \gg 1: \quad \frac{\pi}{2} [1 - \Phi(x)] = \frac{e^{-x^2}}{2x} \left(1 - \frac{1}{2x^2} + \frac{1.3}{(2x^2)^2} - \dots \right).$$

Tables of these functions exist in Jahnke-Emde, "Funktionstafeln," Leipzig, 1933, p. 98.

For a given α , the fraction of monomeric elements existing as components of t -mers can be found by substituting (17) into

$$F_t(\alpha) = \frac{t N_t(\alpha)}{N \sum p n_p} = \frac{t N_t(\alpha)}{N \mu_1} \quad (18)$$

Average Molecular Weights of the Degraded Material.—The formulas for the distribution of molecular sizes of degraded material that we have derived so far are functions of the initial distribution and the degree of depolymerization, α . In most problems it would seem that this form of a result is of little value because one usually cannot measure α directly. However, when it is possible to determine any one of the average molecular weights of the partially depolymerized system, α can be found as a function of that average molecular weight, and then the history of the reaction can be followed by making molecular weight observations at various stages of the degradation process.

The relationship between "number average" molecular weight, M_n^* , and α is immediately apparent from the definition of M_n^* , for $M_n^*/m =$ average number of monomeric elements in a chain, that is

$$M_n^* = \frac{\text{Total number of monomeric elements in the system}}{\text{Total number of molecules in the system}}$$

Since the total number of monomeric elements is conserved during the reaction (*i. e.*, bonds internal in monomeric elements remain intact and only bonds connecting monomeric elements are split) the total number at any time is the same as that in the initial material; that is, $\sum p n_p = \mu_1$. Now the number of bonds in a $(p+1)$ -mer is p , thus the number of molecules whose source was $(p+1)$ -mers is $(1 + \alpha p)n_{p+1}$, and the total number of molecules in a system with the degree of depolymerization α is $\sum (1 + \alpha p)n_{p+1} = \sum [(1 - \alpha) + \alpha(p+1)]n_{p+1} = 1 - \alpha + \alpha\mu_1$. Therefore

$$M_n^*/m = \mu_1/[1 + \alpha(\mu_1 - 1)] \quad (19)$$

In an initially homogeneous distribution with $\mu_1 = p+1$

$$M_n^*/m = (p+1)/(1 + \alpha p)$$

which checks with the corresponding formula derived in reference 3.

To calculate the "weight average" molecular weight, M_w^* , at high degrees of depolymerization, we make the following observations. In the case of a system in which all initial molecules are

$(p+1)$ -mers, when α and p are sufficiently large so that $(1 - \alpha)^p \ll \alpha(p+1)$

$$\begin{aligned} M_w/m &\sim 1 + 2(1 - \alpha)[\alpha(1 + p) - 1]/\alpha^2(1 + p) \\ &= 1 + 2(1 - \alpha)/\alpha - 2(1 - \alpha)/\alpha^2(1 + p) \\ &\sim -1 + 2/\alpha \end{aligned}$$

Suppose p is about 200. If α is as little as 0.2 $2/\alpha - 1 = 9 \gg 2(1 - \alpha)/\alpha^2(1 + p) = 1.6/8 = 0.2$

Thus with initial chain lengths > 200 , and $\alpha > 0.2$, M_w^*/m is independent of the initial chain length. This means, when a system with molecules of various degrees of polymerization > 200 is depolymerized until $\alpha > 0.2$, M_w^*/m becomes independent of the initial distribution and

$$M_w^*/m \sim -1 + 2/\alpha \quad (\alpha > 0.2) \quad (20)$$

the next approximation being obtainable by subtracting $2(1 - \alpha)/\alpha^2\mu_1$.

At low degrees of depolymerization the corresponding derivation is more complicated because one must evaluate directly

$$M_w^* = \frac{\sum N_t M_t^2}{\sum N_t M_t} = \frac{m}{N \mu_1} \sum t^2 N_t \quad (21)$$

using the expression for N_t given in equation (17). The value of $\sum t^2 N_t/N$ is calculated in the appendix (iii) and its substitution in (21) yields

$$M_w^*/m = \frac{\left[\alpha\mu_1(2 - \alpha) - 2(1 - \alpha) \left(1 - \sum_{t=1}^{\infty} n_t(1 - \alpha)^t \right) \right]}{\mu_1\alpha^2} \quad (22)$$

When $n_t = 1$ if $t = p+1$ and zero otherwise, $\mu_1 = p+1$ and

$$\frac{M_w^*}{m} = \frac{\alpha^2(1 + p) + 2(1 - \alpha)[(1 - \alpha)^{p+1} - 1 + \alpha(p+1)]}{\alpha^2(p+1)}$$

which agrees with the formula for the weight average molecular weight of an initially uniform system.³

In an almost normal initial distribution

$$\frac{M_w^*}{m} = \frac{1}{\mu_1\alpha^2} \left\{ \alpha\mu_1(2 - \alpha) - 2(1 - \alpha) \left[1 - \sum_{t=1}^{\infty} (1 - \alpha)^t \frac{e^{-(\mu_1 - t)/2\sigma^2}}{\sigma\sqrt{2\pi}} (1 - \frac{\lambda_3}{3! \sigma^3} H_3 \left(\frac{\mu_1 - t}{\sigma} \right)) \right] \right\} \quad (23)$$

Application of equation (ix) of the appendix simplifies this to

$$\frac{M_w^*}{m} = \frac{(2 - \alpha)}{\alpha} - \frac{2(1 - \alpha)}{\mu_1\alpha^2} \left\{ 1 + \left[1 + \right. \right.$$

$$\frac{\lambda_3}{3!} \log^3(1 - \alpha) \Big] \exp. \left[\frac{\sigma^2}{2} \log^2(1 - \alpha) + \mu_1 \log(1 - \alpha) \right] \Big\} \quad (24)$$

As $\alpha \rightarrow 0$, $\log(1 - \alpha) \sim -\alpha$, and

$$\frac{M_w^*}{m} \sim \frac{(2 - \alpha)}{\alpha} - \frac{2(1 - \alpha)}{\mu_1 \alpha^2} \left\{ 1 + \left(1 - \frac{\lambda_3}{3!} \alpha^3 \right) \exp. \left(-\mu_1 \alpha + \frac{\alpha^2 \sigma^2}{2} \right) \right\} \quad (25)$$

Using equation (19) or (23) one can determine α from a measured average molecular weight (as discussed in reference 3, p. 724, when M_w^* is the measurable variable, α is most easily found by graphical means) and substitution of the α value into (17) or (18) indicates the molecular size distribution. Figure 2 shows the degradation curves of an initially normal molecular size distribution and emphasizes the transition from one sharp distribution to another.

A method to decide whether a given reaction proceeds with random splitting of bonds as discussed in this paper would be to measure both M_w^* and M_n^* at various stages of degradation, and then compare the measured M_w^* values with those calculated from (23) using the α values derived from (19).

Time Dependence of α .—To express the time dependence of α we shall make the assumption that throughout the depolymerization process the rate at which bonds are broken is proportional to the number of uncut bonds.⁵ In this case $dB/dt = -\lambda B$, if B is the number of uncut bonds at time t and λ is a degradation constant. Thus

$$B(t) = Ne^{-\lambda t} (\mu_1 - 1) \quad (26)$$

since the total number of bonds in the undegraded system ($t = 0$) is $N \sum n_p (p - 1) = N(\mu_1 - 1)$. Now the total number of bonds split at the end of time t is

$$B(0) - B(t) = N(\mu_1 - 1)(1 - e^{-\lambda t})$$

Therefore

$$\alpha = \frac{N(\mu_1 - 1)(1 - e^{-\lambda t})}{N(\mu_1 - 1)} = 1 - e^{-\lambda t} \quad (27)$$

The degradation constant, λ , for a given reaction can be evaluated by observing average molecular weights at various times, finding the corresponding α 's from (19) or (22), and applying

$$\lambda = - (1/t) \log(1 - \alpha)$$

One can express the size distribution or average molecular weights of a partially degraded system as a function of the time by substituting (27) in

(5) A similar discussion of this problem has been made by W. Kuhn, *Ber.*, **63**, 1503 (1930).

(14), (19), etc. Some other aspects of the kinetics of depolymerization, such as the probability of a given number of bonds being broken in a given time, follow immediately from the solutions of the corresponding problems in the theory of radioactive disintegrations.⁶

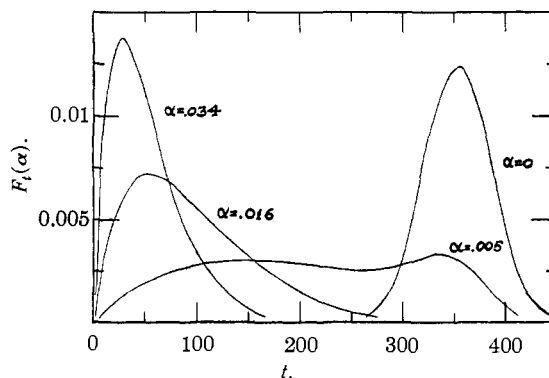


Fig. 2.—Fraction of monomeric elements existing as components of t -mers for various α 's in a system that originally had a normal distribution of molecular sizes ($\mu_1 = 350$ and $M_2/m = 353$).

Appendix

Calculation of $\sum_{t=1}^{\infty} t^2 N_t/N$ and Weight Average Molecular Weights.—From equation (14), if $(1 - \alpha) = \beta$

$$(i) \sum_{t=1}^{\infty} t^2 N_t/N = \sum_{t=1}^{\infty} t^2 n_t \beta^{t-1} + \sum_{t=1}^{\infty} \sum_{p=t+1}^{\infty} t^2 n_p \alpha \beta^{t-1} [2 - (t + 1)\alpha + p\alpha]$$

but for any function $f(p, t)$ (for which the following sums converge)

$$\sum_{t=1}^{\infty} \sum_{p=t+1}^{\infty} f(p, t) = \sum_{t=1}^{\infty} \sum_{p=1}^{\infty} f(p, t) - \sum_{t=1}^{\infty} \sum_{p=1}^t f(p, t)$$

Interchanging the order of summation in the second term:

$$= \sum_{t=1}^{\infty} \sum_{p=1}^{\infty} f(p, t) - \sum_{p=1}^{\infty} \sum_{t=p}^{\infty} f(p, t)$$

Thus

$$(ii) \sum_{t=1}^{\infty} \sum_{p=t+1}^{\infty} t^2 n_p \beta^t [2 - (t + 1)\alpha + p\alpha] = \sum_{t=1}^{\infty} \sum_{p=t+1}^{\infty} t^2 \beta^t n_p (2 - \alpha - t\alpha + p\alpha) - \sum_{p=1}^{\infty} \sum_{t=p}^{\infty} t^2 n_p \beta^t [2 - (t + 1) + p\alpha]$$

Now $\sum_{p=1}^{\infty} n_p = 1$; $\sum_{p=1}^{\infty} p n_p = \mu_1$. Using the fact that

$$\sum_{t=p}^{\infty} t^n \beta^t = \left(\beta \frac{\partial}{\partial \beta} \right)^n \sum_{t=p}^{\infty} \beta^t = \left(\beta \frac{\partial}{\partial \beta} \right)^n \frac{\beta^p}{1 - \beta}$$

(6) See, for example, Ruark and Devol, *Phys. Rev.*, **49**, p. 355 (1936).

we have

$$\sum_{l=p}^{\infty} l^2 \beta^l = \frac{\beta^p}{(1-\beta)^3} \{ p^2 + \beta(-2p^2 + 2p + 1) + \beta^2(1-p)^2 \}$$

and

$$\sum_{l=p}^{\infty} l^3 \beta^l = \frac{\beta^p}{(1-\beta)^4} \{ p^3 + \beta(1+3p+3p^2 - 3p^3) + \beta^2(4-6p^2+3p^3) + \beta^3(1-p)^3 \}$$

Substituting these expressions in (ii), and (ii) in (i)

$$(iii) \quad \sum_{l=1}^{\infty} l^2 N_l / N = \mu_1(2-\alpha)/\alpha - 2 \left(1 - \sum_{p=1}^{\infty} n_p \beta^p \right) (1-\alpha)/\alpha^2$$

For degrees of depolymerization sufficiently small to make $(\alpha\mu_1)^2$ much less than $\alpha\mu_1$

$$\sum n_p \beta^p = \sum n_p (1 - \alpha p + \alpha^2 p(p-1)/2 - \dots) = 1 - \alpha\mu_1 + \alpha^2(\mu_2 - \mu_1)/2! - \alpha^3(\mu_3 - 3\mu_2 + 2\mu_1)/3! + \dots$$

and

$$(iv) \quad \sum_{l=1}^{\infty} l^2 N_l / N \sim \mu_1 + \mu_1(1 - \alpha) \left(\frac{\mu_2}{\mu_1} - 1 \right) \left[1 - \frac{\alpha}{3} \left(\frac{\mu_3 - 3\mu_2 + 2\mu_1}{\mu_2 - \mu_1} \right) + O[(\alpha\mu_1)^2] \right]$$

So (iii) and (iv) imply

$$(v) \quad \frac{M_w^*}{m} = \frac{\alpha(2-\alpha)\mu_1 - 2(1-\alpha) \left(1 - \sum_{p=1}^{\infty} n_p \beta^p \right)}{\mu_1 \alpha^2}$$

and for very small α

$$(vi) \quad \frac{M_w^*}{m} \sim 1 + \left(\frac{\mu_2}{\mu_1} - 1 \right) (1-\alpha) \left[1 - \frac{\alpha}{3} \frac{(\mu_3 - 3\mu_2 + 2\mu_1)}{(\mu_2 - \mu_1)} + \dots \right]$$

Replacement of the μ 's by the corresponding functions of average molecular weights describes M_w^*/m as a function of the degree of depolymerization and of the initial average molecular weights.

In an initially almost normal distribution

$$(vii) \quad \sum_{p=1}^{\infty} n_p \beta^p = \sum_{p=1}^{\infty} \beta^p \frac{e^{-(\mu_1-p)^2/2\sigma^2}}{\sigma\sqrt{2\pi}} \left(1 - \frac{\lambda_3}{3! \sigma^3} H_3 \left(\frac{\mu_1 - p}{\sigma} \right) \right)$$

If α is small enough to make the use of this sum necessary, we can replace the summation operation by an integration, and since $\exp. \{ -(\mu_1 - p)^2/2\sigma^2 \} \rightarrow 0$ very rapidly as p becomes small, we can take the limits of integration as $-\infty$ and $+\infty$. Therefore

$$\sum_{p=1}^{\infty} n_p \beta^p = \int_{-\infty}^{\infty} \frac{e^{-(\mu_1-p)^2/2\sigma^2 + p \log \beta}}{\sigma\sqrt{2\pi}} \left[1 - \frac{\lambda_3}{3! \sigma^3} H_3 \left(\frac{\mu_1 - p}{\sigma} \right) \right]$$

Letting $c = \mu_1 + \sigma^2 \log \beta$ and $x = p - c$

$$\sum_{p=1}^{\infty} n_p \beta^p = e^{c^2 - \mu_1^2/2\sigma^2} \int_{-\infty}^{\infty} e^{-x^2/2\sigma^2} \left[1 + \frac{\lambda_3}{3! \sigma^3} H_3 \left(\frac{\sigma^2 \log \beta + x}{\sigma} \right) \right] dx$$

$$(viii) = e^{1/2 \sigma^2 \log^2(1-\alpha) + \mu_1 \log(1-\alpha)} \left[1 + \frac{\lambda_3}{3!} \log^3(1-\alpha) \right]$$

Thus the weight average molecular weight of an initially almost normal system is

$$(ix) \quad \frac{M_w^*}{m} = \frac{(2-\alpha)}{\alpha} - \frac{2(1-\alpha)}{\mu_1 \alpha^2} \left\{ 1 + e^{1/2 \sigma^2 \log^2(1-\alpha) + \mu_1 \log(1-\alpha)} \left[1 + \frac{\lambda_3}{3!} \log^3(1-\alpha) \right] \right\}$$

As $\alpha \rightarrow 0$, $\log(1-\alpha) \sim -\alpha$, and

$$(x) \quad \frac{M_w^*}{m} \sim \frac{2-\alpha}{\alpha} - \frac{2(1-\alpha)}{\mu_1 \alpha^2} \left\{ 1 + \left(1 - \frac{\lambda_3}{3!} \alpha^3 \right) \exp. (-\mu_1 \alpha + \alpha^2 \sigma^2/2) \right\}$$

Summary

In a polydisperse system of long chain molecules of the same general structure with a single maximum molecular size distribution, this distribution will not deviate radically from a normal one. With this in mind a general distribution function (which shows deviations from normal) is derived in terms of three measurable average molecular weights.

A theory of depolymerization of an arbitrary distribution of high polymers is developed statistically under the assumption that all bonds connecting monomeric elements in the system have the same probability of being broken. The molecular size distribution at any time is given as a function of the initial distribution and of the fraction of bonds split.

Under the assumption that the rate at which bonds are cut is proportional to the number of uncut bonds in the system, the time dependence of the degree of depolymerization is discussed.